

Pacifichem 2000 Symposium on Plasma Chemistry and  
Technology for Green Manufacturing, Pollution Control  
and Processing Applications

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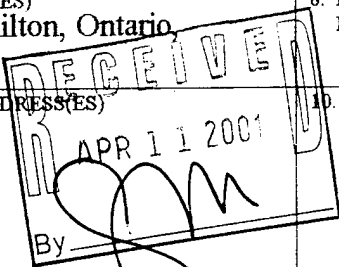
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13. ABSTRACT (Maximum 200 words)

Plasma chemistry and technology represents a significant advance and improvement for green manufacturing, pollution control, and various processing applications. The US Army as well as the DoD have a very large number of operational and military needs that can be addressed by state-of-the-art plasma technologies. These include clean-up/restoration of a wide range of contaminated sites (soils and groundwater), control of release of toxic vapors during peacetime operations at military bases and depots, as well as combat applications such as decontamination of personnel clothing and materiel contaminated by CBW agents. The Pacific Basin Chemical Societies jointly organize a major Congress every five years. The Pacificchem 2000 was held from December 14-19, 2000 in Honolulu, HI. This Congress consists of over 120 symposia, amongst them the Symposium on Plasma Chemistry and Technology for Green Manufacturing, Pollution Control, and Processing Applications. This symposium was aimed at highlighting many of the new and exciting developments in the plasma chemistry field beyond the more traditional and mature fields of semiconductor and materials processing. This symposium was focus on three areas: Pollution Control with Standard and Hybrid Non-Thermal Plasmas; Green Chemical Synthesis, Conversion, and Materials Modification; and Plasmas in Food and Agricultural Applications.

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## **PROJECT DESCRIPTION**

### **Pacifichem 2000**

Pacifichem 2000 was organized jointly by the American Chemical Society, Canadian Society of Chemistry, the Chemical Society of Japan, the New Zealand Institute of Chemistry, and the Royal Australian Chemical Institute. In the 2000 Congress, more than 120 symposia were organized in 10 areas (Appendix 1). Each symposium attended by 30-100 attendees where Pacifichem 2000 was held December 14-19, 2000 in Honolulu, HI, USA and approximately 7000 people from 45 different countries was attended.

### **Background on Plasma Applications and Some Specific DoD Applications**

Non-thermal plasmas (NTPs) represent a promising technology for the destruction of various toxic gases released during military and civilian operations. The history of treating hazardous and toxic chemicals with NTPs goes back over twenty years demonstrating military use for destroying toxic chemical warfare agents with electric discharge reactors and civilian applications for treating flue gases ( $\text{SO}_x$  and  $\text{NO}_x$ ) from electric power plants and other installations (e.g., steel mills) with electron beams; indeed the electric-discharge-driven NTP-initiation of chemical reactions has a history of nearly one and one-half centuries. NTPs also show promise in the control of toxic gas released from military industrial facilities that treat energetics (i.e., propellants and pyrotechnics) and produce nitro-aromatics and nitramine or nitrite esters, and that process volatile organic compound (VOC) waste from painting/removal and solvent cleaning. The treatment of these wastes produces  $\text{NO}_x$ . Recently, NTPs have been applied to the reduction of hazardous gases in jet engine and cruise missile test cells (JETC and CMTC) where large amounts of nitric-oxides ( $\text{NO}_x$ ) are emitted along with various hydrocarbon (HC) gases on an episodic basis. In April of this year a small, pilot-scale field demonstration using a trailer-mounted reactor and funded by SERDP was carried out at Tinker Air Force Base near Oklahoma City. The field work involved the treatment of a portion of an exhaust stream from a small jet engine test facility and concentrated on the removal of nitric oxide ( $\text{NO}_x$ ) from the exhaust stream. Preliminary data analysis shows promising performance (in some cases  $> 80\%$   $\text{NO}_x$  removal).

### **Symposium 211**

Symposium 211 is titled "Plasma Chemistry and Technology for Green Manufacturing, Pollution Control, and Processing Applications". It is located in the Environmental Chemistry Area. This symposium has been organized by Dr. A.W. Miziolek, Prof. J-S Chang, and Dr. K. Mizuno, and consists of two sessions: Plasma Pollution Control (being held on Thursday, December 14) and Green Chemistry and Novel Applications (being held on Friday, December 15). Each session consists of 9 invited and 3 contributed oral presentations (Appendix II) from 6 countries. Approximately 70 people from 12 different countries per session were attended. The abstracts of each presentation will be published in a conference proceedings abstract book. In addition, the organizing committee plans to publish full papers in a special issue of an archival journal (e.g. J. Advanced Oxidation Technologies), or the Mercel Dekker Inc. New York Symposium book series. In a similar symposium in Pacifichem 1995, the organizers (2 of whom are organizing this symposium) arranged for a special issue of the journal Combustion Science and Technology (Vol. 133, No. 1-3, 1998).

## Summary of Symposium Presentation (by J. Hoard and edited J.S. Chang)

Plasma discharges along with catalysts are being investigated as a possible lean-NO<sub>x</sub> control system. The plasma is oxidative, converting NO to NO<sub>2</sub> and partially oxidizing HC. A number of researchers are active in this emerging technology area. John Hoard (Ford) presented an overview of current technology including zeolite and alumina catalysts. High NO<sub>x</sub> conversion over a wide temperature range is an advantage; energy costs and low space velocity are drawbacks. Further increases in efficiency are needed for future NO<sub>x</sub> standards.

A. Mizumo (Toyohashi University of Technology) is studying plasma-catalyst systems. They have tested both single stage (packed bed) and two stage (plasma followed by catalyst). Plasma-alumina removed 60% NO<sub>x</sub> at 100-150°C with methanol reductant at 6000-12000 SV and about 60 J/L. A Co-ZSM catalyst in a two stage system at 30 J/L gave 60% NO<sub>x</sub> conversion with addition of NH<sub>4</sub> at 150°C.

Ogata (National Institute for Resource and Environment – NIRE – Japan) is using a plasma-zeolite reactor to study benzene removal. There is both storage and oxidation of the benzene. Song (Korea Institute for Research) has done similar work. Zeolites improved propane and benzene removal efficiency more than did Pt, alumina or glass. Futamura (NIRE Japan) also looked at VOC removal, with plasma and catalyst combinations. MnO<sub>2</sub> catalysts were tested for benzene and other VOCs. Benzene adsorbs on the catalyst, and is oxidized by the plasma products.

A pair of projects looked at reduction of NO<sub>x</sub> from jet engine test cells. Miziolek (US Army Research Lab) developed a CFD model of the NH<sub>4</sub> radical-injection plasma system that includes plasma and chemical effects. Chang (McMaster University) reported on slip stream tests on jet engine test cell exhaust. Nearly complete NO<sub>x</sub> and SO<sub>x</sub> removal were shown, with the reaction products being particulates that can be recycled as fertilizer. Cost (\$/gm-NO removed) is about 1/4 that of conventional systems for high flow rates.

Yamamoto (Osaka Prefecture Univ.) uses plasma with addition of NaSO<sub>3</sub> to remove NO<sub>x</sub> from flue gas. 30-140 J/L is needed for 90% NO<sub>x</sub> removal.

K. Mizumo (NIRE Japan) is studying fluorocarbon decomposition by plasma torch. Large scale systems are already in use in Japan. Energy consumption is 6-7 times lower than oil-flame incineration. In a similar vein, Chang (National Central University, Taiwan) studied dioxin emissions from waste incinerators. Appropriate additives and correct choice of operating temperature can produce very low dioxin levels.

Oda (University of Tokyo) is studying VOC removal, including CFC, halogenated VOC, and aromatics. Various discharge reactors have been tested along with catalysts.

Ono (Musashi Institute of Technology) looked at waste plastic disposal in a plasma. Water and Ar are passed through plasma at a few Torr, and then powdered plastics are added. The products are useful for recycling as plastics. This is favorable compared to methods which completely oxidize the plastic. The plasmas breaks plastic bonds, which are then capped by H to improve selectivity.

Urashima (McMaster University) reported removal of PFCs in a full scale packed bed reactor incorporating adsorbent material. Zeolite catalysts were used in the plasma bed packing. The combination of plasma chemistry and zeolite storage was very effective in removing  $\text{NF}_3$ ,  $\text{SiF}_4$  and other PFCs.

Gunderson (USC) and Ohkubo (Oita University) each reported LIF imaging studies of NO around plasma discharge streamers. This is very difficult diagnostics, since the needed laser stimulation energy can affect the gas and therefore the streamer.

Yamano (Nagasaki Univ.) is studying NO decomposition with a microwave plasma with SiC or graphite blocks. Plasma power is very high in these experiments.

Ohkubo (Oita University) reported experiments with a packed bed reactor using  $\text{BaTiO}_2$  pellets. The pellets were heat treated in various ways. NO conversion is best when the pellets have the best balance of dielectric constant and surface area.

Kato (University of Tokyo) reported using a plasma in  $\text{CH}_4$ -Ar mixtures to make acetylene. 95% selectivity was obtained with 40-50% methane conversion.

Hoffman (Cal Tech) studied destruction of *E. coli* bacteria in a water plasma system. The uv light generated by the discharge seems to be the main mechanism killing the bacteria. However, the destroyed bacteria release compounds which absorb UV light, limiting maximum effectiveness. Plasma UV generation is more efficient than UV light bulbs. Sato (Gunma University) looked at plasma treatment of waste water. This can reduce VOCs, dye, and bacteria more effectively than ozone. Locke (Florida State) looked at degradation of organic compounds by aqueous plasma. Phenol and microorganisms can be destroyed. Some catalysts can assist the process.

## **Sessions: Plasma Chemistry and Technology for Green Manufacturing, Pollution Control, and Processing Applications**

### ***Plasma Catalyst for Diesel emission reduction***

John Hoard, Ford Research Lab (USA)

A brief overview of plasma-catalysis applied to diesel engine exhaust was given. The gas phase plasma discharge is an oxidizing environment. Electrons dissociate  $\text{O}_2$  creating O radicals that react with the HC present, starting a reaction chain creating aldehydes, OH radicals, and peroxy radicals. The latter react very quickly with NO. The net effect is that engine-out NO is oxidized to  $\text{NO}_2$  with small amounts of  $\text{HNO}_3$  and  $\text{CH}_3\text{ONO}_2$ . The HC is partially oxidized. The gas phase plasma alone does not remove NOx, although various measurement problems can cause it to appear to do so. Some chemiluminescent NOx analyzers are subject to interference from species produced in the plasma such as formaldehyde.

When the gas after the plasma passes over catalysts, it is possible to have NOx conversion to  $\text{N}_2$ . One catalyst that has been extensively studied is sodium-substituted zeolite-Y ( $\text{NaY}$ ). This material can convert 50-60% NOx over a wide temperature range, from about 150C to 300C. The NOx which remains after the catalyst is NO.  $\text{HNO}_3$  and  $\text{CH}_3\text{ONO}_2$  are not present after the

catalyst. The catalyst has no effect on the exhaust when plasma is off. It also has little effect on the HC and aldehyde, so an oxidation catalyst is needed downstream in a practical system.

Cu-ZSM<sub>5</sub> has widely been reported to be a lean NO<sub>x</sub> catalyst. However, it is not effective in combination with plasma in this low temperature range.

The Ford-GM-DaimlerChrysler USCAR Low Emission Partnership is working with Pacific Northwest National Lab and the US Department of Energy. This group has developed a proprietary, non-precious metal zeolitic catalyst "B" which has better NO<sub>x</sub> conversion than NaY, reaching 60-70% over the range 150C-300C.

Another class of catalyst that works well with plasma is alumina. An alumina catalyst converts NO<sub>x</sub> 70-80% from 250C to 500C. A dual bed of Catalyst B followed by alumina converts 60-80% from 150C to 500C. Like the other catalysts, this data is around 10,000 hr<sup>-1</sup> space velocity (SV), a rather low value.

Full conversion in these simulated gas blends costs about 15 J/L energy input, which roughly costs 3% fuel consumption. Since the reaction requires HC addition to the diesel exhaust, the total cost is about 5.5%.

There have been reports of plasma-catalyst systems which can remove >80% particulate matter from diesel exhaust. Figures were shown courtesy of AEA Technology. Their recent SAE paper (June 2000) is a good description of issues related to soot in plasma. It isn't clear yet whether one can remove NO<sub>x</sub> and particulates in the same system with a reasonable size and power consumption.

This emerging technology is evolving very rapidly. Current efforts are working to raise the NO<sub>x</sub> conversion to the 90% or better required for future emission regulations, understand the effects of soot on the plasma, and develop suitable devices for larger scale testing.

### ***Decomposition of NO by microwave-induced plasma under atmospheric pressure***

Toshiyuki Yamano, Nagasaki Univ. (Japan)

The work is aimed at simultaneous NO<sub>x</sub> and PM removal with microwave induced plasma.

2.45 GHz microwave radiation excites SiC or graphite blocks in the gas flow. The plasma is formed at the points of the conductive blocks. NO-methane mixture in an Ar/O<sub>2</sub> stream is the test gas. (Ar is easier for plasma than air!)

At 120 ml/min flow rate, NO decomposition required >20W; N<sub>2</sub> was formed, without oxygen in the gas. When O<sub>2</sub> present, N<sub>2</sub> formation drops strongly. Thus, you need a reducing agent when O<sub>2</sub> is present. So, methane was tried.

Emission spectrum from the plasma shows bands attributed to OH, C<sub>2</sub>, H<sub>α</sub> as well as O and Ar. This shows that NO and methane bonds are broken at 80 W.

With enough methane you can get some NO conversion to N<sub>2</sub>, around 40%. If one needs 80 W at 120 ml/min, this is 40K J/L – an extremely high power input for practical uses.

With a graphite block, there is still some 40% conversion with  $O_2$  and without methane; presumably, some of the carbon is being used as a reductant. In a  $N_2$  carrier, conversion was lower than in Ar; probably back channels, plus vibrational loss.

For PM, a PM trap is used. Offline, it is microwave regenerated. If we also adsorb  $NO_x$ , perhaps we can decompose both. The offline regeneration will potentially permit sufficiently large J/L inputs without excessive fuel economy penalty.

## **Removal of dilute benzene using zeolite-hybrid plasma reactor**

Atushi Ogata, National Institute for Resource and the Environment (Japan)

Past methods include ferroelectric packed bed reactors. However, for benzene they are non-selective. In this work, zeolites were used to adsorb benzene in a bed mixed with  $BaTiO_3$ .

Molecular sieve zeolites MS-3A, -4A, -5A and 13X were used. These have pore sizes in a range which prohibits some of the sample gases (benzene, NO,  $N_2O$ ,  $CO_2$ ) from entering the pores.

A mix of 200 ppm benzene, 0.5% water in air at 200 cc/min was tested. Flow ran until the storage was saturated, then plasma was turned on for 30 minutes and then off again. With MS-13X we never saw benzene in gas phase downstream of the catalyst because it could fit into the pores. Smaller pores allow some benzene to pass.

The oxidation products  $CO/CO_2$  show for most materials the  $CO/CO_2$  increased when power on. All but 3A continued to show  $CO/CO_2$  after power off, with a decay time constant  $\sim 10$  minutes. This suggests some adsorption of COx. TPD was used to test for adsorption. The larger pore materials offgass COx during the TPD, more so from materials with larger pores.

The hybrid reactor was 1.4-2.1X more effective than conventional reactor. Formation of  $NO_x$  was lower.

It seems to be easier to decompose benzene outside pores than inside.

A cyclic adsorb/regenerate cycle might be more efficient. With the same input power, 2.3X the oxidation products were formed compared to constant operation.

Discussion:

Is there a surface deposit? *After a long discharge, oxidation products in gas reach a steady state. About 10% of carbon is not found in the outlet gas, so as much as 10% stays in zeolite, but we did not see a visible change.*

## **Pulsed plasma for diesel emission reduction**

Martin Gunderson, University of Southern California (USA)

Reviewed USC work on:  $NO \rightarrow NO_2$  conversion using pulsed plasma; LIF studies of the process; power conditioning; some new applications. Most of the presentation reviewed work previously reported.

Transient plasma requires less than 100 nsec pulses. Understanding the NO effects requires understanding the test conditions: power type, HC, NO concentrations, temperature, etc.



Electric arcs are popular but inefficient. You prefer a transient discharge with a larger fraction of energetic electrons. Electron avalanche/streamer formation (0-30 nsec) produces ions, UV photons, molecular excited states, electron attachment/detachment, etc. The streamer is surrounded by a high field which accelerates electrons.

The reactor was modeled with a Monte Carlo method for ion & radical production, Poisson for fields. A "BiThermal Plasma" phase (usually called nonthermal) has hot electrons and cooler ions/radicals/molecules. Radical chemistry occurs over a longer time scale.

Most of the electrons have too-low energy to help much; they just vibrate  $N_2$ .

Streamers vary depending on polarity and gas composition. The modeling is subtle and difficult!

LIF measurements were made in plasma converting NO to  $NO_2$ . Transient plasmas seem to be better than long-pulse plasmas.

There has been extensive development of the power supply. Line impedance must match the supply for these fast pulses. A solid state supply stores 15 mJ in capacitance per pulse, and delivers 9 (9/15 = 60% efficiency!).

Some new areas of transient plasma are being investigated; "talk to me later"!

Discussion:

Streamer morphology changes in a few nanosec, depending on polarity.

### ***Contamination control of air by using nonthermal plasma with catalysts***

Tetsuji Oda, University of Tokyo (Japan)

Atmospheric pressure plasma is being studied for removal of VOC, which might include CFC, halogenated VOCs, aromatics, and others.

Reactors include modified electrostatic precipitators, barrier discharge, surface discharge, and various power supplies.

Surface discharge is used to make ozone, and these work well. One can also do a packed bed with catalyst in it. We use a stainless steel bolt inner electrode in a cylindrical packed bed reactor. In some cases, a cordierite monolith is just downstream of the plasma. We have also used a DBD with pulse source; we have tried coating catalysts on the barriers ( $TiO_2$ , CuZSM). Without HC, the DBD was not so good, but OK with HC.

Pulse supplies work well, but in many reactors a 50-60 Hz AC supply works equally well. We have tried many types.

LIF has been used to image  $NO^*$ , or OH, in needle-needle or needle-barrier discharge.

To improve reactor efficiency you must: reduce miscellaneous losses, have good plasma uniformity, and avoid pass-tunnels. Fast rise time pulses are preferred.

For TCE decomposition, 50 Hz is more efficient than 500 Hz. A bolt-type center electrode is better.

What does a catalyst do? We are running tests, but have many questions. TCE decomposition over  $V_2O_5/TiO_3$  catalysts was tested; plasma maintains efficiency better than non plasma. But, we sometimes see different byproducts from catalyst than without plasma. We are concerned about desorption.

Our main background is electrical not catalytic!

In packed bed reactors, catalysts may change the discharge mode; is it really catalysis or just different discharge?

### ***Synergetic effects of nonthermal plasma and catalysts on the decomposition of pollutant gases***

Y. H. Song, Korea Inst. res. Metal and Machinery (S. Korea)

Can catalysts/adsorbents reduce plasma power cost for VOC treatment?

A packed bed reactor is used, a wire-in-cylinder design with packing of alumina, glass, Pt-alumina, molecular sieve MS 3A, 4A, or 5A.

Benzene stores on glass & alumina; plasma-catalyst efficiency best-to-worst is in the order Pt > MS 5A > alumina > glass. Similarly, for propane 5A >> glass, alumina

The packing material changes the plasma properties so we need to check power consumption and discharge characteristics.

We measure power by Lissajous figure or by voltage times current calculated in the oscilloscope. Both methods got the same power measurement.

When calculating eV/molecule energy cost, MS 5A is better than glass, alumina, or Pt for both propane and benzene. To see if this is due to different plasma conditions, we looked at UV light emission. The ratio of two N<sub>2</sub> peaks allows estimation of electron energy. Comparing MS 5A to glass, the MS has higher emission intensity but lower electron energy. Electron energy was 9-10 eV, while we expected ~5 eV; we don't know why yet. It seems likely that there is a measurement error.

The different packing materials change the relation between power and voltage applied.

For TCE removal, 90% removal is obtained with alumina at 150 J/L, Pt 132, glass ~50 J/L to get 90% conversion. However, the byproducts vary for different packing materials.

Packing materials reduce power required for toluene and propane removal, but not for TCE; the byproduct distribution is changed. This may be due to either changed plasma conditions or catalytic chemistry; much more investigation is needed! We need to work on carbon balances.

*Quartz tube was 30 mm dia, length 30 cm, residence time <1 sec.*

## **Silent discharge model development for NO conversion**

Andrzej Miziolek, US Army Research Lab; (USA)

Defense facilities must comply with air emissions regulations for NO<sub>x</sub> from jet engine test cell facilities. DoE also has VOC abatement needs.

Nonthermal plasma has “hot” electrons with “cool” neutrals and ions. The advantages compared to other methods are in-situ generation of reactants, no need to heat gases for reaction, and ability to control power deposition.

This was a subset of the main program, and we set out to do a CFD model with detailed chemical mechanism to simulate a DBD reactor. The device was a planar reactor with one electrode transparent. The barriers are UV quality glass. This was made under a SBIR grant. It allows optical diagnostics. There are also windows allowing line of sight measurement through the plasma parallel to the barriers. A picture shows rather uniform glow. There are many streamers distributed well through the volume.

Mechanisms used in the model are those proposed by Herron based on Lowke and Morrow. 32 species, 88 reactions are included. Dry air, moist air, and propene were cases of interest.

ARL-NSRG2 code for CFD was used. This includes gas dynamics, chemistry. The user specifies number & location of discharges. Discharges create large gradients in species concentration, which promptly react and diffuse. O concentrations in wet air are 2X lower than in dry air.

Army Research Lab, LANL, McMaster, & NIST cooperated in a project to control NO<sub>x</sub> from jet engine test cell. See more below (Prof. Chang and Dr. Urashima). But, the money ran out before careful comparison of the CFD model to data!

Discussion:

What happens if you go to higher pressures? *We didn't attempt it because it is not appropriate for our application. One expects the kinetics to change a lot.*

## **Small pilot scale field demonstration of the control of atmospheric emissions from jet engine test facilities using a corona radical shower nonthermal plasma reactor**

Jen-Shih Chang, McMaster University (Canada)

This is the experimental work for the project described above by Miziolek. We are focusing on the jet engine test cell. NO<sub>x</sub> is a few up to 35 ppm depending on operating modes. There are also PM, 5 ppm SO<sub>x</sub>, 20 ppm VOC and ~1 ppm N<sub>2</sub>O in the exhaust. Exhaust temperature runs 400-600C. However, it is down to 50C at the cell chimney where the aftertreatment is applied. PM is 800 microgram/m<sup>3</sup> at full load.

A slip stream is taken through a corona radical shower reactor, the catalyst, then electrostatic filter. The corona radical shower injects a gas through a plasma into the exhaust gas. The addition gas is N<sub>2</sub>/O<sub>2</sub>/NH<sub>3</sub> so we generate N and NH radicals to remove NO<sub>x</sub>.

The system used only a few hundred watts up to 125 Nm<sup>3</sup>/hr. NO conversion is nearly complete; NO<sub>x</sub> conversion is 80% decreasing with increasing flow rate to 40% at 100 Nm<sup>3</sup>/hr. N<sub>2</sub>O is also removed but at lower efficiency. SO<sub>x</sub> is removed effectively. The reaction products are nitrates and sulfates which can be used for fertilizer.

This technique was compared to pulsed corona, e-beam, and conventional methods for emission control. The corona shower system used less energy. Total annual operating cost is also attractive. In high flow rate systems, the plasma systems are about 1/4 the cost of conventional systems in \$/gm-NO.

No ozone or ammonia slip was measurable in the test cell demonstration. Traces of aldehydes (<0.5 ppm) and CO (<5 ppm) were present in the effluent.

Discussion:

If NO<sub>x</sub> increased to 200-300 ppm as in a typical power plant, is it still economical? *Yes, plasma is much better. We published some data last year. Plasma is 3X cheaper than pulse corona, 20X cheaper than conventional NO<sub>x</sub>/SO<sub>x</sub> control*

### ***Decomposition of fluorocarbons by an inductively coupled RF plasma torch***

Koichi Mizuno, National Institute for Resources & Environment, (Japan)

About 550 tons of CFCs are recovered per year in Japan, and much more is out there in refrigerators etc. Only 20-50% of this is recovered. We need facilities to destroy the recovered CFCs.

Methods of destruction are incineration with waste or in manufacturing, submerged combustion, plasma (inductive RF, microwave, or arc), and catalysts. There are currently 34 CFC destruction facilities in Japan. The plasma facilities are near Tokyo.

Destruction can be accomplished using O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, methane, or CaO (in a cement kiln producing CaF<sub>2</sub>). For some CFCs you must have O<sub>2</sub>.

The rf plasma torch inductively couples energy into the plasma through a double glass wall with cooling water between the tubes. Plasma temperature is about 10,000 C. Products are scrubbed with water at the outlet.

We have to worry about byproduct formation as well as destruction efficiency. We get >99.9% destruction efficiency for CFC-12 and Halon-1301. Efficiency is not a strong function of feed rate. When Halon is destroyed by incineration, you get byproducts which we do not get when we use the rf plasma torch.

The largest unit built to date is 100 kW. It can handle >1K L/min. 99.999% destruction of >80 kg/hr CFC is achieved.

The waste water from the scrubber does not contain unacceptable levels of byproducts. Dioxin emission is very small. The plasmas torch is considered a commercial technology for CFC destruction. Such torches have been in use since 1994.

Energy consumption is 6-7 times lower than incineration in an oil flame. 7380 kJ/kg CFC is the plasma energy required.

Recovery of CFCs and Halons is required both for ozone hole protection and for greenhouse gas reduction. The plasma torch is an attractive means of doing so.

Discussion:

Did you ever try TFE destruction? *no*

### ***Evaluation of dioxin emissions from two MSW incinerators in Taiwan***

Moo Been Chang, National Central University, (Taiwan)

Potential dioxin emissions are a concern from incinerators. There are currently 11 large scale solid waste incinerators in Taiwan, with 36 more under construction. By 2006 >90% of solid waste will be incinerated.

Taiwan has established emission standards for incinerators. These are much lower than US standards, and are the world's most strict.

We tried to evaluate 2,3,7,8- substituted dioxin removal efficiency. EPA method 23 was used for sampling. Particle bound and gaseous dioxins are collected

The incinerator generates power, and then the gas goes thru an ESP for particulate removal, followed by a wet scrubber. For this experiment, samples could be taken for analysis.

Another unit tested used a cyclone collector followed by filter bags. Activated carbon and alkaline agents can be used for dioxin and VOC removal.

Dioxin concentration was measured before the pollution control system for two operating units. In unit MWI-A the dioxin concentration increased rather than decreasing when passing through the air pollution control system! The main reason is that the temperature is close to 250C, so the ESP can generate dioxins. Unit MWI-B T=218C) without activated carbon injection, there is a small removal percentage of dioxins. With carbon, 98.3% dioxin removal was measured.

Carbon removes less-chlorinated compounds better than more-chlorinated ones. This seems to correlate with vapor pressure of the components.

Dioxin gets adsorbed on small particles, and removal of these needs to be improved from current particulate removal systems.

Discussion:

What happens after the carbon adsorbs dioxin? *We have to get rid of it.*

### ***Kinetics and mechanisms of E. coli disinfection in a pulsed plasma discharge reactor***

Michael Hoffman, Cal Tech (USA)

We looked at plasma to inject ions into water to remove industrial and hazardous waste, including TNT. We wondered if this would also kill organisms in water.

A pulsed power supply is used. Tantalum electrodes are used. The discharge is into water. The water must have some electrical conductivity. Steam bubbles are generated and the main

discharge takes place in water vapor. The plasma lasts ~1 msec. The discharge emits UV lightened also creates a shock wave, causing cavitation.

Disinfection could come by means of UV light, or by the shock wave which may damage bacteria. The steam bubble can also disinfect.

The reactor is about 3-4 liters with some air in the cavity.

TNT was destroyed by 207 discharges of 1 KJ each. Nitrates were released, and the carbon is converted to CO<sub>2</sub>.

Anthrax and its spores is a possible target for destruction. Temperature in the plasma reaches as high as 50K degrees.

E Coli ATCC 25922 was tested. We found that the number of cells decreased with plasma treatment but only approached zero asymptotically. If there are too many organisms present, the energy required to kill them goes up sharply; we don't now why yet.

What mechanism kills the bacteria? We looked at ultrasonic 20 KHz energy to see if it is the plasma generated shock wave. In that experiment a larger initial bacteria count means shorter kill time, opposite what was seen in the plasma.

A UV light shows a similar disinfection time to the plasma time. This suggests that it is the UV light which is killing the bacteria. Perhaps when many bacteria are present at the start, their destruction products absorb UV light and limit the destruction efficiency. We find Beta-D-galactosidase levels (from bacterial walls) in the liquid rise with plasma time. This suggests also some mechanical damage to the cells.

We added a UV absorber to the water. With this, the cells are not killed. Thus, we know that UV light is the main effect. We think that the cells release something which absorbs UV.

We can build a better reactor as a thin film device to improve efficiency.

Discussion:

Why not just use a UV lamp? *We were actually interested in some other organisms which are not susceptible to UV.*

You may need to have a sharper pressure rise rate.

*In the thin film you won't have the shock wave effects. The plasma systems are more efficient in making UV in water than conventional light bulbs. The UV is formed right in the water here. It does need some redesign based on our experience with this reactor.*

## **Removal of NO<sub>x</sub> from diesel engine exhaust using plasma-chemical process.**

Toshiaki Yamamoto, Osaka Prefecture Univ. (Japan)

A Plasma-chemical hybrid method uses plasma for NO → NO<sub>2</sub>, then chemical removal of NO<sub>2</sub>. Generally, NO → NO<sub>2</sub> is hard by plasma alone; at high power you get byproducts. The hybrid process uses Na<sub>2</sub>SO<sub>3</sub>:

Na<sub>2</sub>SO<sub>4</sub> is the final product, water soluble non-toxic.

Engine exhaust is filtered and dried by collector and silica bed before plasma treatment.

NO<sub>x</sub> varies with load, 150-600 ppm. At light load, NO can convert to NO<sub>2</sub> in the plasma but complete conversion causes some byproducts. At high load, there is not enough power to convert all NO. NO removal is not strongly affected by temperature or humidity, plotted against voltage.

With the chemical process added, ~90% NO<sub>x</sub> removal is seen. 30 to 140 J/L is needed for 90% NO<sub>x</sub> removal, depending on NO<sub>x</sub> input level.

Discussion:

Where is a practical application of this? *Co-generation etc; we can't use a wet process for mobile applications.*

You may have a problem to operate at such low temperatures.

### **Low temperature NO<sub>x</sub> reduction process by combination with pulsed discharge and catalyst**

Akira Mizuno, Toyohashi Univ. Technology (Japan)

There are two ways to combine plasma & catalyst: single stage packed bed, or two stage with plasma followed by catalyst. In the single stage, high energy particles can interact with the catalyst. In the two stage system, the plasma converts NO to NO<sub>2</sub> before catalyst; the catalyst does more conventional SCR. SCR with ammonia works better with NO<sub>2</sub> than with NO, so the plasma improves low temperature operation. We are looking for the reduction pathway for NO<sub>x</sub> removal at low to medium temperature.

Simulated gases are blended; the single stage reactor is a concentric cylinder with catalyst packing and pulse power supply. No water is added according to the diagram shown. C<sub>2</sub>H<sub>4</sub> or NH<sub>4</sub> are used as reductant. FTIR, NO<sub>x</sub> and SO<sub>x</sub> monitors measure the results.

A mechanical chopper generates pulse excitation; students can't break them! Square wave 30-40 Hz, 20 KV pulses result. The spark gap switch gives 20 nsec rise time.

For a single stage reactor with gamma alumina (270 m<sup>2</sup>/g) without additives, the maximum NO<sub>x</sub> removal was not very good, about 20%. We added methanol, and removal went up to 60%. Temperature = 100 and 150C.

This result was stable up to 30 hr operation. 500 ppm NO<sub>x</sub> reduced to 250. SV = 6000 – 12000, energy 60 kJ/m<sup>3</sup> (=60 J/L). After operation, examined pellets for residue by washing and ion chromatography. Sum of residual plus measured NO<sub>x</sub> divided by input NO<sub>x</sub> gives 15% without additives, and 80% with methanol addition. The surface turned a bit yellow without methanol; no color change with methanol.

Ethanol was somewhat better as a reductant than methanol, and increasing reductant concentration improved performance.

Lower SV improves efficiency. Higher surface area catalyst (also alumina, 200 m<sup>2</sup>/gm) gave better removal with methanol but not with ethanol.

In a two stage system 400 ppm NO input, at 30 J/L almost all NO → NO<sub>2</sub>. Co-ZSM5 monolith was used. Almost all output NO<sub>x</sub> was NO, conversion of NO<sub>x</sub> was about 60% when NH<sub>3</sub> was injected between plasma and catalyst. Better results were obtained after modifying for better gas

mixing.  $\text{NH}_3$  slip was <30 ppm at 150C for a 6 hour test, 27 J/L, 200-400 ppm  $\text{NH}_4$  and 400 ppm NO input.  $\text{NO}_x$  conversion was ~85%. This shows SCR can be done at 150C.

Energy cost for the single stage reactor with ethanol was 27.5 eV/mol, and for the two stage with  $\text{NH}_3$  and with  $\text{C}_2\text{H}_4$  in the plasma was 25 eV/mol destroyed. These are approaching reasonable energy costs.

Up to 5% water, there is little effect on the plasma-catalyst.

### ***Ab Initio calculation of ion-induced water nucleation by dividing model of cluster energy***

Masayuki Itoh, Doshisha Univ., (Japan)

Plasma may generate clusters (particles) by ion nucleation. This may make diesel soot reduction difficult. A new model for ion-induced nucleation was developed.

Most calculations show monotonic increase of energy to the cluster size with no qualitative agreement with classical nucleation theory.

We start with T and P, use Monte Carlo condition of embryo (# of molecules and basic cell size). Then MO calculation is done with GAMESS, calculating energy of embryo core, surface, and gas molecules. This leads to  $\Delta G$  energy change of embryo.  $\text{Na}(\text{H}_2\text{O})_n^+$  is assumed as embryo.

A potential is assumed for water-water interaction, only for use in the Monte Carlo simulation leading to the initiating cluster. For water-ion nucleation, Kistenmacher parameters are used. A single ion is assumed, and then a periodic boundary condition for water. Otherwise you calculate infinite energy potential!

Clusters develop with water clustered around a  $\text{Na}^+$  ion.

The cluster is divided in three regions: inner cluster diameter, outer diameter, and transition region of outer water molecules. This leads to first minimum in energy in a way consistent with conventional theory.

The free energy versus number of molecules in the cluster has a min at 4-6 molecules, and first max at 9 molecules. The values are a bit different from the classical formulation.

The metastable sizes correspond to a symmetrical structure of the cluster.

These clusters are neither liquid nor solid, but still in quasi-gas phase. This is because the packing of the water molecules is not very dense.

Work is continuing to improve quantitative match of this model to data.

Discussion:

*For different cation initiators, you get a different location of the first minimum in energy*

### ***2-D NO concentration by UV pulse laser LIF diagnostic system in a DC positive streamer corona***

Toshikazu Ohkubo, Oita Univ., (Japan)



We want to gather data to challenge theories! There isn't enough validation of plasma discharge models yet.

One has to understand the interaction between the LIF laser excitation and the luminescence of the discharge. Application of the laser causes an additional streamer if the laser contacts the discharge streamer.

DC discharge in air with 200 ppm NO, with nozzle to mesh electrode geometry and gap >3 cm. Most previous LIF has been done after end of discharge; we left voltage on.

Typical LIF of NO uses 226 nm wavelength to see ground and excited states of NO. The ratio of ground to excited state depends on temperature. Is the nonthermal plasma really low temperature? 193 & 237 nm light can look at excited states.

The discharge is in 1000 ppm NO in N<sub>2</sub> or air.

The NO LIF signal is not linear in the range of 0-1000 ppm, but it is pretty linear up to 200 ppm., using 226.1 excitation and imaging with ICCD unfiltered.

Typical streamers occur about 5kHz without laser due to the 1.6 Mohm series resistor; an added streamer occurs if the laser is fired. We cannot synchronize the laser to the natural discharges.

Laser power can induce added discharges. The probability of such increases with laser power; at the level used, you usually get an added discharge. The streamers travel  $2.5 \times 10^5$  m/sec.

The laser position can be adjusted relative to the electrode. A longer delay between laser shot and streamer occurs if the laser is moved away from the electrodes.

2D images show gradual reduction of NO in the (very slowly flowing) gas volume. After long times, the NO is destroyed outside the streamer region while there remains some NO under the needle, perhaps because of back conversion. The corona creates a flow which improved gas mixing. Temperature is within 10 deg of ambient.

More data will look at 1D data in a corona radical shower to help with modeling.

Discussion:

Why DC instead of pulse discharge? *We are interested in DC positive corona such as corona radical shower systems. In this case we can use DC coronas for very cheap power supply.*

What does the laser do to cause a discharge? *The laser produces some ionization due to high light fluence; I am not sure why. There is an effect of the space charge.*

If you change the excitation frequency does it change the discharge? Are you exciting NO to ionize it, or is it something else? You could tell by "detuning" the laser.

If you have NO<sub>2</sub> present, the laser may dissociate some of it and create NO.

## **Study of waste plastic disposal by means of H<sub>2</sub>O microwave plasma process**

S. Ono Musashi Inst Tech, (Japan)

10 million tons of plastic wastes are generated each year in Japan, of which only 10% are recycled. Of this, 50% incinerated and 40% buried. We are looking for a plastic recycling technology. A water plasma is studied in this case.

The water plasma creates photolysis, pyrolysis, chemical decomposition and physical decomposition all at once. We think that adding H to the decomposition products is suitable in recycling plastic.

Water is used as an H source in the plasma. Methanol, acetone, ethanol and isopropanol are obtained as reaction products according to another group.

Water is added to Ar or N<sub>2</sub> and passed through a microwave cavity. The effluent is passed through a cold trap for product collection. Powdered plastic is added to the gas flow at the plasma exit.

Polyethylene (PE) powder is used. Microwave power 500 W flow 60 cc/min. Powder is added 50 mm after plasma so diagnostics can be used in the reaction. Pressure 1 Torr.

The plasma stimulates  $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$  as verified by observed emission spectrum. Rotational temperature of N<sub>2</sub> molecule is about equal to gas temperature so we use it to measure temp.

Gas temperature is high, 1000-2000 C, increasing with pressure in the range 5-20 Torr. The water is hotter than the N<sub>2</sub>.

Adding plastic to the plasma we see C<sub>2</sub>, CO, CH spectra. CO is not seen if pure N<sub>2</sub> or Ar is used; the CO arises from oxygen in the water.

Decomposition time (time for CH or C<sub>2</sub> spectra to disappear) is minimum at 4 Torr. Plasma electron temperature was 4 eV at lowest press, 3 eV at  $\geq 5$  Torr. Electron density is also higher at lower press. However, N<sub>2</sub> rotational temperature shows a maximum at 4-5 Torr. Thus, minimum decomposition time corresponds to peak gas temperature.

If N<sub>2</sub> or Ar is used without water, you get deposits on the tube walls. With water, the walls are clean.

Discussion:

How important is the energy cost? *I have not worried about it yet; we just started this work.*  
What products did you find? *We didn't analyze yet, but others say methanol, ethanol, acetone, isopropanol.*

## **Wastewater treatment using pulsed discharge in water**

Masayuki Sato Gunma Univ., (Japan)

Some applications of pulse discharges in water are decolorization of dye, nonthermal sterilization, sludge from wastewater, etc.

OH radicals and other species, UV lights and shock waves can reduce organics in water. Dye is exposed to plasma at constant temperature. HV pulsed power is used including rotating double spark gap.

Three discharge modes can be used with point-plane configuration. First, large gap creates streamer discharge. With close gap, streamer with spark. At short gap, spark discharge. We prefer the intermediate, streamer plus spark because it cleans the dye faster.

The rodamine B dye is gradually destroyed; two hours gave a clear liquid. 80% of the dye was removed.

Adding  $H_2O_2$  improved removal rate, especially in spark mode. With  $H_2O_2$ , strong UV light from spark may be most important.

Sterilization of microorganisms was also studied. Yeast cells were killed linearly as the E field strength increases. This could be used for killing microorganisms in milk, juice, etc. The mechanism may be E field destruction of cell membranes.

Reduction of activated sludge was also studied. Water sludge is hard to dispose. Ozone oxidation is being tried. Ozone disrupts cell walls, releasing material which is recycled and consumed by bacteria so there is no waste stream. Thus, no activated sludge is created. Waste water is aerated, then settling tank used to concentrate the sludge, which is then plasma treated and recycled into the aeration tank.

Ozone is less effective than a pulsed discharge. Ultrasound is even more effective. But, the pulse treatment is better at disrupting the yeast cell walls so you can better recycle the intracellular material.

Spark-streamer mode is most effective; spark next; streamer least effective.  $CO_2$  is generated by bacteria digestion during the process. The ultrasound process shows the best  $CO_2$  generation (highest activity), closely followed by pulsed discharge. The ultrasound may be energy intensive however, so the pulsed treatment may be advantageous.

Finally, a double sparking phenomenon was observed in distilled water. There are two steps to the break down from streamer to spark discharge. One current spike appears about 50 microsec before a second, larger spike. A drop in applied voltage accompanies the first spike across the cell. Light is emitted at 309 nm (OH) during break down. This intensity is higher in the first spark than in the second, even though the current is lower. We don't know why yet. We can see two breakdowns from one capacitor discharge.

Summary: there are several potential applications of pulsed discharges in water.

#### Discussion.

Activated sludge contains heavy metals. Does your recycling cause metal condensation or kill the bacteria used? *That problem is present in other methods also. We have no good ideas how to get them out. You can't do 100% recirculation.*

What about cost? *The treatment cell is a bit better than ozone but we don't have exact numbers.*

What frequency was the ultrasonic sound and what power density? *Not my data, I am not sure.*

It took 3 hours at 50 Hz for 200 ml on the dye; you need much faster! *Power level is rather low*

What is the effect of changing the capacitor? *We have only studied a small range. The double sparking gap is sensitive.*

## **Plasma processing technologies for thin-film solar cell production**

Yukumi Ichikawa, Fuji Electric Co R&D, (Japan)

Fuji is studying ozone, nuclear waste and other plasma applications.

To reduce cost of a Si solar cell, large-scale production is required. We are working on a roll-to-roll apparatus by adopting a flexible substrate, and using plasma CVD.

This consists of layers of plastic film polyimide, then metal layers, then Si, then a transparent electrode. A large number of unit cells are connected in series.

A long film roll is used so it can be loaded in a machine for punching, coating etc. Sputtering and plasma CVD are used for the various layers. Laser scribing is used for interconnections, then cut and stacked. The cells are 40x80 cm, and we can get 200 volts in sunlight so you can connect direct to the inverter.

In conventional systems the film moves continuously. Our new apparatus uses stepped motion. We have plasma CVD and sputtering all in one machine. By stepping the motion, we can control the pressure of each stage independently. Sputtering and plasma steps require different pressures. When the film is stopped, we press down the ground electrode, forming a pressure seal where required. 13 CVD chambers and two sputtering stations are included in one machine. The machine is about 20 meters long.

The large number of stations is required to improve performance. Multi-junction cells are used by varying the composition in the vertical direction. These are Si-Ge triple cells. We obtain 10% conversion efficiency, or about 100 W per m<sup>2</sup> in sunlight.

A demonstration building has been built with cells on the roof providing 2.9 kW. The cells are made in the form of roofing tiles. These do not have glass and look rather like conventional roofing material. The flexible cells are made like roofing tile. They can also be pasted on a wall, or a ship cabin, or an arched roof.

Discussion:

*Crystalline cells are around 15-20% efficient, but 2-3X price.*

*Long-term stability is good because plastic is sandwiched in metal. Expect >15 yrs.*

## **Degradation of organic compounds by aqueous-phase pulsed corona discharge**

Bruce Locke, Florida State Univ. (USA)

Our work is similar to Prof. Sato's. We are using HV pulsed electrical discharges at 60 Hz, point-plane geometry, around 1 J/pulse (larger than Hoffman's).

These create OH radicals, H radicals and H<sub>2</sub>O<sub>2</sub>. Phenol and microorganisms can be destroyed.

We can add activated carbon particles in the medium in previous experiments. Today I will describe addition of zeolites for dye removal.

Another hybrid reactor is where the plane electrode is in air above water. This creates both aqueous and air discharges. We form ozone in air and  $\text{H}_2\text{O}_2$  in water.

For water discharge, we get OH,  $\text{H}_2\text{O}_2$ , and H radicals. But,  $\text{H}_2\text{O}_2$  is formed both directly and by recombination of OH radicals. Iron can facilitate  $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$  or  $\text{HO}_2 + \text{O}$  (Fentons reaction).

UV formation is a strong function of water conductivity.

We have done calculations of  $\text{H}_2\text{O}_2$  formation vs. conductivity. Higher conductivity reduces  $\text{H}_2\text{O}_2$  formation.

Phenol was decomposed in this system. We form catechol, hydroquinone, resorcinol but then they degrade; the model describes the phenol degradation but the byproducts are not right yet. There are byproduct interactions. The important reactions are  $\text{H}_2\text{O}_2 \rightarrow \text{H} + \text{HO}_2$  and  $2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}$ . The Fenton reaction and direct phenol + OH are also important.

In the hybrid water-oxygen system we can get ozone. OH attack on phenol is important, ozone less so. But, both can react with byproducts. At 200 KJ/L destruction takes about 45 min. We remove total organic carbon better in this hybrid system than in water only discharges.

We added some zeolite in some dye destruction experiments. Mordenite  $\text{NH}_4$  or H-Y was used. We tried adding  $\text{H}_2\text{O}_2$  without corona and with zeolites but saw no removal. Seven dyes were tested.

All the dyes are too large to enter the zeolite pores except one dye molecule which might partially enter.

High color removal was obtained for all dyes. Some dyes form toxic byproducts, but they are not significant here. Total carbon was removed well for some dyes but not all. In some cases the two catalysts behaved quite differently.

Discussion:

*We have not tried a wide range of water conductivities in the hybrid system. Gap is about 1 cm, and that is rather sensitive. The ground electrode is porous carbon which is very useful as it makes many point sources.*

*Can you compare your  $\text{H}_2\text{O}_2$  method with remote plasma method where  $\text{H}_2\text{O}_2$  is made externally and injected to water? My numbers suggest UV/ $\text{O}_3$  numbers for phenol are 20 eV/mol which is close to our value. This is expensive for  $\text{H}_2\text{O}_2$  production but it is in-situ.*

### **Removal of mixed PFCs by a full scale by a full scale ferro-dielectric packed bed nonthermal adsorbent hybrid reactor**

Kuniko Urashima, McMaster Univ., (Canada)

Greenhouse gasses are a concern.  $\text{CF}_4$  has 6500 times more effect than  $\text{CO}_2$ , and  $\text{NF}_3$  has 8000 times;  $\text{C}_2\text{F}_6$  is also high. We need a way to treat them. We need to destroy at either low or high pressure, or perhaps adsorb them.  $\text{NF}_3$  and  $\text{C}_2\text{F}_6$  are used in semiconductor industries. RF freq low press plasma could be used. Here we use a packed bed reactor with zeolite adsorbent filter.

$\text{C}_2\text{F}_6$ ,  $\text{NF}_3$ ,  $\text{SiF}_4$  and  $\text{CF}_4$  are tested in the experimental mixture. There is a zeolite bed downstream of the packed bed plasma unit. The packed bed is water cooled.  $\text{BaTiO}_3$  beads are

used in the plasma reactor. Gas residence in plasma is 0.4-40 sec. 2000 ppm  $C_2F_6$  + 1000 ppm  $CF_4$  + 1000 ppm  $N_2O$  are input. Plasma alone removed 20-40% of  $C_2F_6$  &  $CF_4$ , improving to >90% with zeolite trap at low flow. Removal decreases at high flow. The zeolite increases removal here too. After plasma,  $CO_2$ ,  $C_2F_4$ ,  $CHF_3$  and other products are seen. Most of those are adsorbed by the zeolite.

A mix of  $NF_3$  &  $SiF_4$  was tested. Plasma removes  $NF_3$  nearly 90%; zeolite is needed for best efficiency. Zeolite does a large fraction of the removal for  $SiF_4$ . Again, the plasma creates byproducts which are adsorbed by the zeolite.

Discussion:

*$N_2O$  is increased a bit over the plasma but adsorbed by zeolite.*

*Is the power supply important? Would short pulses help? In this reactor with ferroelectric beads, the reactor temperature is probably more important. Probably yes, we are doing it.*

### ***Influence of pellet properties on NO<sub>x</sub> removal in a Packed Bed plasma reactor***

T. Ohkubo, Oita Univ., (Japan)

We are testing these reactors for VOC and for NO<sub>x</sub>.

Packed bed ferroelectric pellet reactors create intense plasma around pellet contact points. The surface materials take part in the reactions.

We made  $BaTiO_3$  pellets in our lab, 20mm dia x 5 mm pellets, then crushed the sintered tablets to get about 3 mm pellets.

Mesh electrodes are used upstream and downstream of the bed, 70.5 mm dia 10 mm long. NO in simulated dry air, measured with NO<sub>x</sub> analyzer and GC. Used 25 kHz AC power supply, power measured at transformer *input*.

200 NO and 20%  $O_2$  in  $N_2$ , 1 L/min were used unless noted.

The result (plotted as NO versus KV) depends on the sintering temperature of the beads. Lower temperatures are better down to 600C, although that is better than no sintering at all. Sintering at 1000C nearly kills activity; NO may increase at higher voltages.

Dielectric constant of the beads is low if sintered below 1000C, then very high above that. At the same temperature, the surface area of the pellets drops markedly. At lower temperature, the structure is cubic, but goes to tetragonal after high temperature sintering.

The maximum NO<sub>x</sub> reduction follows the specific surface area rather closely.

Testing for a long time causes changes; the NO<sub>2</sub> output gradually increases; the input NO may have been adsorbed in the pellets in shorter tests.

$N_2O$  and ozone are generated if you put in too much power.

600 C sintering is best, but the reaction is oxidation of NO to NO<sub>2</sub>, clouded by storage.

We put various catalysts on the BaTiO<sub>3</sub> pellets using ceramic paste. Pt, V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, CuO, ...

This has a strong effect on reactor performance. Pt increased oxidation. Catalysts in order of oxidation activity were: Pt > V<sub>2</sub>O<sub>5</sub> > Ni > ceramic coating. This will have changed the dielectric constant also.

In this case, even after 15 hours, the ceramic pellets with Pt are still emitting low NO<sub>2</sub>. BET method was used to check adsorbed NO<sub>2</sub>; it is small compared to converted NO<sub>2</sub> so there is real conversion it seems.

Discussion:

*Temperature was room temperature, but the reactor self heats.*

How much Pt was coated? *Whole surface covered by ceramic, then unknown amount, probably 1%*

What is the velocity? *Velocity and area are important.*

### **Control of VOC decomposition behavior in air with silent discharge and catalysts**

S. Futamura, National Inst for Resource & Environment, (Japan)

We have looked at plasma followed by catalyst, or plasma in catalyst with photocatalyst. We think that the oxidation power of active oxygen species is critical. We do not use adsorbents; we use a dry scrubber as an acid gas scavenger.

We have looked at DBD, PB and pulsed wire in tube.

MnO<sub>2</sub> catalyst was used for benzene removal; this is the data shown today. Air, N<sub>2</sub>, VOC, and water are mixed, then passed through the PB reactor. GC analysis was used to measure products.

A graph was shown for removal of several VOCs vs. kJ/L in dry air. Benzene was less reactive than olefinic VOCs. TCE is converted better in dry air than in N<sub>2</sub>, suggesting active oxygen would help.

Can we use ozone and a catalyst to decompose benzene? We used a plasma reactor followed by a bed of MnO<sub>2</sub>. MnO<sub>2</sub> was better than other catalysts tested. This is an inexpensive catalyst. Benzene adsorbs on the MnO<sub>2</sub> surface. We saturated the cat with benzene then started plasma. At 2 kJ/l the plasma alone removed 30% of the benzene, while the plasma-catalyst removed >90%. This is a very good result. This only happens in air, not in N<sub>2</sub> carrier, so we think the cat is promoting oxidation with ozone. After the MnO<sub>2</sub>, ozone is gone and NO<sub>2</sub> is not present. It took 8 moles of ozone per mole of benzene, so there may be loss mechanisms or other active O species.

O(<sup>3</sup>P) would be much more active than O<sub>3</sub>; it may be that O<sub>3</sub> is decomposed on the MnO<sub>2</sub> to generate O(<sup>3</sup>P) radicals which are much more reactive with benzene.

MnO<sub>2</sub> is much better than MnO or Mn<sub>2</sub>O<sub>3</sub>.

It takes some time for benzene conversion to reach a maximum. After the reaction, an air purge carries CO and CO<sub>2</sub> off for some time. This suggests storage of benzene on the surface. Benzene conversion is worse when water is present. The catalyst helps at all humidity levels. This implies

that OH radicals do not help the oxidation. It is likely that the degradation of performance with humidity is due to lower ozone production when water is present.

We can use the catalyst for a rather long time; we are checking the life. Also, we are looking at other cats.

Discussion:

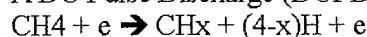
Have you looked at byproducts? *We could not find any by GC or GCMS. There are some deposited carbon fragments.*

## **Methane activation with direct pulse discharge**

Shigeru Kato, Univ. of Tokyo, (Japan)

We would like to convert abundant natural gas into useful chemicals. This can be done by making syngas, by oxidative dehydrogenation, or by direct dehydrogenation. But, these are hard to control and energy intensive.

A DC Pulse Discharge (DCPD) is applied to methane. This causes



The short pulses reduce consecutive decomposition of products.

An axial rod-rod discharge was used. Analysis was by GC-FID, GC-TCD, GC-MS. Experiments were ambient temperature & pressure, no catalyst.

5% CH<sub>4</sub> in Ar was used. Acetylene can be formed at about 95% selectivity with about 40-50% conversion of methane. Current industrial processes convert only about 30% of methane to acetylene.

The problem is carbon deposition on the electrodes which can be stopped by adding a little oxygen. 10% O<sub>2</sub> caused CO production along with acetylene, and no carbon deposition. C<sub>2</sub> selectivity drops to 65%.

Selectivity was insensitive to electrode gap.

We also looked at syngas production. Varying O<sub>2</sub> partial pressure, more oxygen increases CO & CO<sub>2</sub> but CO selectivity decreases with CH<sub>4</sub>/O ratio.

Adding water decreases acetylene formation and increases CO selectivity and H<sub>2</sub> formation.

Adding CO<sub>2</sub> to methane causes more CO formation and less C<sub>2</sub>. So, the dilution with CO<sub>2</sub> is not much use.

Adding Ni<sub>0.03</sub>Mg<sub>0.97</sub>O catalyst increased CO selectivity to 99% for methane/CO<sub>2</sub> reforming.

Various other reactions are possible by controlling the operation conditions. We also produced CH<sub>2</sub>O and CH<sub>3</sub>OH.

Discussion:

Have you checked if the carbon you found in your process was carbon black or what? *Black soot on both electrodes. It could grow to short the electrodes.*



Using DBD can make methanol with zeolite cat. Have you tried? *No, we haven't. We did look at some other cats for various purposes. Pt/SiO<sub>2</sub> helped for C<sub>2</sub>H<sub>6</sub> ethane*

## Appendix.1



**The 2000 International Chemical  
Congress of Pacific Basin Societies**  
Honolulu, Hawaii, USA ♦ December 14-19, 2000

### SYMPOSIUM ORAL SESSION PROGRAM

The program is subject to change. The final schedule will be published Wednesday, July 5<sup>th</sup>.

Contributed oral and poster sessions will be added in the July 17 issue of C&EN and on PacifiChem 2000 web page.

#### key code:

Thu=Thursday      Sun=Sunday      AM = morning  
Fri=Friday          Mon=Monday      PM = afternoon  
Sat=Saturday      Tue=Tuesday      Eve = evening

#### hotel:

HHV=Hilton Hawaiian Village      RI=Renaissance Ilikai  
HR=Hyatt Regency                  SMS=Sheraton Moana Surfrider  
RH=Royal Hawaiian                SW=Sheraton Waikiki

#### AREA 1: Agrochemistry – including agriculture, cellulose, carbohydrate, pulp, and paper chemistry      HHV

005, Immunochemical Biomonitoring for Environment Chemicals; Hideo Ohkawa; Sun AM, PM, Eve  
006, Molecular Designs of Food Proteins for Industrial Applications; Akio Kato; Mon AM, PM; Tue AM  
111, Functional Food Ingredients: Trends and Prospects; Feriedoon Shahidi; Thu AM, PM; Fri AM, Eve  
134, Utilization of Biomass for the Production of Chemicals in the Twenty First Century; Jon Meister; Thu AM, PM; Fri AM, PM  
139, Quality of Fresh and Processed Food; Arthur Spanier; Fri PM; Sat AM, PM  
145, Industrial Enzymes; Srinivasan Damodaran; Fri PM; Sat AM, PM  
152, Chemical Modification, Properties and Usage of Lignin; Thomas Hu; Sat AM, PM  
153, Lignocellulosics Science and Technology: From Laboratory to Market; David Hon; Sun PM; Mon AM, PM  
165, Chemical Ecology and Biochemistry of Plant Resistance to Diseases and Nematodes; Robert Stipanovic; Thu AM, PM; Fri AM  
192, Bioconversion of Lignocellulosics to Ethanol and CoProducts; John Saddler; Mon Eve; Tue AM  
202, Food and Beverage Antioxidants in Health and Disease; Joe Vinson; Sun AM, PM

#### AREA 2: Analytical Chemistry – including clinical, electrochemical, and trace analysis      RI

021, Electrochemical Sciences; Koichi Aoki; Mon AM, PM  
026, Liquid-Liquid Interfaces in Analytical Sciences; Hitoshi Watarai; Thu AM, PM; Fri AM  
031, Soft X-Ray Spectroscopy: New Evaluation of Chemical Composition of Functional Materials; Hisanobu Wakita; Sun AM, PM  
074, New Wave of Analytical Reagents for Symbiotic Human Life with Nature; Mizuo Maeda; Sat AM, PM  
075, Frontiers of Spectroscopic Analysis of the Brain; Hideaki Koizumi; Thu AM, PM; Fri AM, PM  
076, New Optical Probes for Chemical and Biochemical Analyses; Koji Suzuki; Mon PM  
113, Ultrasensitive Chemical Measurement and Characterization; Edward Yeung; Thu AM, PM; Fri AM, PM  
117, Separation Science: Trends for the New Century; Robin Rogers; Fri PM, Eve; Sat AM, PM; Sun AM  
121, Novel Measurements of Gas Phase Ions; John Traeger; Sat AM, PM; Sun AM  
124, Elemental Mass Spectrometry for a New Millennium; Naoki Furuta; Sun PM; Mon AM, PM; Tue AM  
137, MicroBioanalytical Chemistry: Separations and Manipulations of Micron Size Domains; J. Michael Ramsey; Sat AM, PM; Sun AM, PM; Mon AM  
154, Chemical and Biochemical Sensors; Raoul Kopelman; Thu AM, PM; Fri AM, PM, Eve; Sun Eve  
159, Recent Developments in Field Analysis; Janusz Pawliszyn; Mon AM, PM  
171, Raman Spectroscopy: Coming of Age in the New Millennium; Robin Turner; Fri AM, PM; Sat AM, PM  
204, Chemical Sensors Based on Chemical Recognition; Eric Bakker; Sun AM, PM, Eve  
214, Recombinant Proteins in Analytical Chemistry; Sylvia Daunert; Mon AM, PM

#### AREA 3: Bioscience and Technology – including microbial and pharmaceutical chemistry      HHV

038, Pyridoxal Biocatalysis: Fine Catalytic Mechanism and Application; Kenji Soda; Mon AM  
040, Chemical Regulation of Bioreactions and Biorecognitions; Makota Komiyama; Thu AM, PM  
046, Peptide Chemistry as Life Molecular Science; Hisakazu Mihara; Sat AM  
047, Biomineralization: Controlled Bio-Architecture by Inorganic and Organic Molecules; Tadashi Matsuhaga; Sat AM, PM  
061, Advances in Solid State NMR of Biomolecules and Materials; Akira Naito; Sun AM, PM, Eve; Mon Eve  
063, Bioengineering of Extremophiles and Extremozymes; Ichiro Okura; Fri AM, PM  
073, Astrobiology and Origins of Life; Kensei Kobayashi; Mon AM, PM; Tue AM

- 129, Medical Applications of Nucleic Acid Molecules; Siew Ping Ho; Sun AM, PM  
 158, Biomolecular Structure and NMR; Raymond Norton; Sun PM; Mon AM, PM, Eve; Tue AM  
 170, Biosynthesis of Natural Products; Craig Townsend; Thu AM, PM; Fri AM, PM  
 185, Evolution of Enzyme Function; John Gerlt; Sat PM; Sun AM  
 186, Xenobiotic Enzymology; Richard Armstrong; Thu AM, PM  
 187, Multiple Solutions to the Same Chemical Problems; Rowena Matthews; Fri AM, PM  
 188, Nucleic Acid-Protein Complexes as Drug Receptors; Laurence Hurley; Sat AM, PM  
 194, Metal Thiolate Clusters in Biological Systems: The Biochemistry and Chemistry of Group 11 and 13 Metals and Their Reactions with Metallothioneins, Phytochelatins, Gamma-EC Peptides and Related Metal Complexes; Martin Stillman; Fri AM, PM  
 196, Environmental Biotechnology: Bioremediation and Bioprevention; Murray Moo-Young; Sat AM, PM  
 205, Glycobiology; Curtis Brewer; Mon AM, PM, Eve  
 220, Advances in Biochemical Production Technologie; Mark Marten; Sun AM, PM, Eve; Mon Eve

**AREA 4: Chemistry and the Community – including chemical education, chemical economics and business, and public education and outreach**

**HR**

- 041, Environmentally Benign Chemistry Including Microscale and Smallscale Laboratory; Kazuko Ogino; Fri AM, PM; Sat AM  
 051, Changing Chemical Scene in the Pacific Basin; Naoya Yoda; Mon AM, PM; Tue AM  
 059, International Relationship in Chemical Education; Yoshito Takeuchi; Sat AM, PM  
 120, Testing with Technology; Charles Atwood; Mon AM  
 143, Teaching Aspects in Chemistry: Curriculum Developments in Analytical Chemistry; Gary Christian; Thu AM, PM; Fri AM  
 150, Chemistry for Elementary Schools; Sue Ann Berger; Sun AM, PM, Eve  
 184, International Perspectives of Graduate Education; P. Wyn Jennings; Fri Eve  
 190, Metrology, Standards, Testing, Quality (MSTQ): Keys to the Future for the Chemical Enterprise; Nina McClelland; Sun AM, PM, Eve  
 195, Catalysis and Catalytic Processes for Efficient Chemical Synthesis; Harold Kung; Fri AM, PM; Sat AM  
 206, Research Supported Teaching/Learning Innovations; Diane Bunce; Mon AM, PM  
 207, Laboratory Education in the 21st Century; Thomas Wildeman; Sun PM  
 216, Multimedia and Visualization in Chemistry for the Major and the Non-Science Major; Zafra Lerman; Sun AM

**AREA 5: Environmental Chemistry**

**RI**

- 112, Environmental Chemistry of Main Group Organo-Metallics; Rorbert Pellenberg; Sat AM, PM  
 115, Photochemistry of Freshwater and Marine Environments and its Impact on Biogeochemical Cycles; David Kieber; Thu AM, PM; Fri AM, PM  
 116, Environmental Applications of Ionizing Radiation; William Cooper; Sun AM, PM, Eve; Mon AM, PM, Eve; Tue AM  
 118, Sampling and Analysis for Verification with the Chemical Weapons Convention; Lawrence Keith; Sat AM, PM  
 142, Characterization, Performance and Fouling of Water Treatment Membranes; Amy Childress; Mon AM, PM; Tue AM  
 155, Chemical and Biochemical Technology for Improving the Environment; Kiran Kadam; Sun AM, PM  
 211, Plasma Chemistry and Technology for Green Manufacturing, Pollution Control, and Processing Applications; Andrzej Miziolek; Thu PM; Fri PM

**AREA 6: Inorganic Chemistry – including geochemistry and nuclear chemistry**

**SW & SMS**

- 002, Selective Chemical Transformation on Late Transition Metal Complexes; Sanshiro Komiya; Sat AM, PM; Sun AM, PM  
 009, Selective Catalysis for Environmental Applications; Yasuhiro Iwasawa; Thu AM, PM; Fri AM, PM  
 013, Multifunctionality of Inorganic, Organic, and Their Hybrid Solids, Part 1. Electric Conductivity and Related Properties; Susumu Kitagawa; Sun PM; Mon AM  
 014, Multifunctionality of Inorganic, Organic, and Their Hybrid Solids, Part 2. Molecular Magnetism and Related Properties; Toshiaki Enoki; Sat AM, PM; Sun AM  
 015, Recent Progress in Rare Earth Chemistry; Gin-ya Adachi; Thu AM, PM  
 017, Polyoxometalate Chemistry for Nano-Composite Design; Toshihoro Yamase; Fri PM; Sat AM, PM  
 018, Advances in Inorganic Fluorine Chemistry: New Synthetic Methods, Applications in Industries and Material Sciences, and Computational Aspects; Tsuyoshi Nakajima; Sun AM, PM, Mon Eve  
 019, Inorganometallic Chemistry of Group 13-16 Elements; Hiroshi Ogino; Sat AM, PM; Sun AM  
 023, New Trends in Biofunctional Metal Complexes; Shigenobu Yano; Thu AM, PM; Fri AM  
 027, Nuclear Hyperfine and Exotic Particle Techniques for Studying Chemical States; Masuo Takeda; Mon PM, Eve; Tue AM  
 028, Metal Complexation in Colloid and Polymer Systems; Tohru Miyajima; Sat AM, PM  
 032, Fundamental Studies on Coal for the New Century; Masahi Iino; Fri AM, PM, Eve  
 034, Main Group Chemistry I: Advances in Synthesis, Theory and Applications; Kin-ya Akiba; Fri PM; Sat AM, PM  
 037, Structure and Dynamics of Solute-Solvent Interactions; Hitoshi Ohtaki; Thu AM, PM  
 043, Oxygen Activation by Metalloproteins and Their Models; Masatatsu Suzuki; Fri AM, PM; Sat AM, PM

- 049, Inorganic Organometallic and Biological Chemistry of Metal Sulfides; Kazuko Matsumoto; Sun PM; Mon AM, PM  
 067, Environmental Chemistry and Microbiology of Actinides; Zenko Yoshida; Sat AM, PM  
 070, Organometallic Chemistry of Early Transition Metals and Lanthanides; Tamotsu Takahashi; Mon AM, PM; Tue AM  
 072, Bio-inspired Molecular Design of Multinuclear Metal Centers; Mitsuhiro Shionoya; Sun AM, PM  
 101, Metal-Mediated Nucleophilic Cleavage of Nucleic Acids; James Bashkin; Mon PM; Tue AM  
 105, Main Group Chemistry II: Low Valent, Low Coordination Number and Cluster Compounds; Penelope Brothers; Sun AM, PM, Eve; Mon AM  
 106, Reservoir Geochemistry; R.J. Hwang; Sun AM, PM, Eve  
 107, Chemistry and Application of Metal Complexes of Mixed-Donor Multidentate Ligands; Craig Jensen; Sun AM, PM, Eve; Mon AM  
 109, Twenty Years of Organic Superconductors: New Materials - New Insights; Urs Geiser; Mon PM; Tue AM  
 130, New Developments and Directions in Inorganic Charge Transfer Complexes; Clifford Kubiak; Thu AM, PM; Fri AM  
 135, Radioisotope Production and Applications in the New Century; Dennis Phillips; Sun AM, PM  
 148, Fundamental and Technological Advances in Actinide Chemistry; R.G. Haire; Fri AM, PM  
 151, Electron and Atom Transfer Chemistry of the Late Transition Metals; Gregory Hillhouse; Thu PM; Fri AM, PM  
 166, Chemistry of Inorganic Thin Film Formation; Martin Zinke-Allmang; Mon AM, PM, Eve; Tue AM  
 169, Science with Radioactive Beams; ManYee Tsang; Sun Eve; Mon AM, PM, Eve  
 180, New Materials from Organometallic and Coordination Chemistry; M. David Curtis; Thu AM, PM; Fri AM, PM  
 212, Molecular Recognition of Anions and Cations; Anthony Baker; Mon AM, PM; Tue AM  
 213, Chemical Effects of Ultrasound; Kenneth Suslick; Mon AM, PM; Tue AM

#### AREA 7: Macromolecular Chemistry

RHV & SMS

- 003, Advanced NMR Characterization of Polymers: Precise Structural Analyses and Molecular Interpretation of Macroscopic Properties; Fumitaka Horii; Thu AM, PM; Fri AM, PM, Eve  
 044, Polymer Thin Film Interfaces; Tisato Kajiyama; Fri PM, Sat AM, PM  
 050, High Performance Polymers; Masa-aki Kakimoto; Sun PM; Mon AM, PM  
 054, Photonic Processes in Polymers and Self-Organized Materials; Tomiki Ikeda; Thu AM, PM; Fri AM, PM  
 055, Structures and Properties of Polymer Alloys; Hirokazu Hasegawa; Sat AM, PM; Sun AM, PM  
 056, Self-Ordering Phenomena in Polymeric Systems: From Microscopic to Mesoscopic Scales; Kenichi Yoshikawa; Sat PM; Sun AM, PM; Mon AM  
 057, Precision Polymerizations and Controlled Supramolecular Architectures; Mitsuo Sawamoto; Thu AM, PM; Fri AM, PM, Sat AM  
 058, Liquid Crystalline Polymers: Self-Organization of Macromolecules with Well-Controlled Orientation and Polarity in the Liquid Crystalline Field; Junji Watanabe; Thu AM, PM; Fri AM  
 068, Photophysics and Photochemistry of Polymeric Materials; Kazuyuki Sugita; Mon AM, PM, Eve  
 102, Reactive Polymer Processing; Warren Baker; Mon PM, Tue AM  
 127, Pi-Conjugated Polymers; Steven Holdcroft; Thu AM, PM; Fri AM, PM  
 149, New Methodologies in Polymer Synthesis; Bing Hsieh; Sat PM; Sun AM, PM; Mon AM  
 157, Aromatic Azo Materials and Applications; Almeria Natansohn; Sat AM  
 177, Self-Assembly in Water-Soluble Polymers; Francoise Winnik; Fri PM; Sat AM, PM  
 193, Dendrimers and Hyperbranched Polymers - Synthesis, Structure, and Properties; Jung-Il Jin; Sat AM, PM; Sun AM  
 197, Characterization and Modeling of Membrane and Barrier Polymers; Benny Freeman; Thu AM, PM; Fri AM  
 203, Associations in Solutions: Amphiphiles, Macromolecules and Colloids; Saad Khan; Mon PM; Tue AM  
 209, Radiation Chemistry of Polymers; David Hill; Sun AM, PM, Eve; Mon AM

#### AREA 8: Medicinal Chemistry

HHV

- 011, Chemistry and Signal Transduction; Mikiko Sodeoka; Mon AM, PM, Tue AM  
 036, Neurochemistry of Excitatory Amino Acids; Yasufumi Ohfune; Sun AM, PM  
 045, Molecular Recognition Using Nucleic Acids and Their Related Substances; Akira Matsuda; Thu AM, PM; Fri AM, PM  
 132, Recent Advances in Protease Inhibitor Design; Patrick Lam; Thu AM, PM  
 140, Mathematical and Computational Aspects of Molecular Design; Dave Winkler; Fri Eve; Sat AM, PM  
 156, Viral Serine Proteases; Dennis Liotta; Fri PM, Eve  
 160, Cysteine Proteases; Peppi Prasit; Fri AM  
 172, Advances in Radiopharmaceutical Chemistry; Henry VanBrocklin; Fri AM, PM  
 173, Alzheimer's Disease: Receptors and Small Molecule Therapies; Donald Weaver; Mon AM, PM  
 174, Radionuclides for Therapeutic Oncology; Suresh Srivastava; Sun Eve; Mon AM, PM, Eve  
 181, Frontiers in Antibiotics: Synthesis, Design and Mode of Action; Robert Williams; Sat AM, PM; Sun AM, PM  
 189, Next Generation Therapeutics; John Kozarich; Sun AM, PM  
 199, Chemical Perspectives on Human Cancer; Lisa Peterson; Sat AM, PM; Sun AM, PM  
 217, MMP Inhibitors; Biswanath De; Sat AM, PM

- 218, Combinatorial and Parallel Synthesis: Applications to Medicinal Chemistry; Andrew Combs; Mon AM, PM; Tue AM  
 219, Novel Mechanisms for the Treatment of Pain; Ed Roberts; Thu AM, PM

## AREA 9: Organic Chemistry

HHV

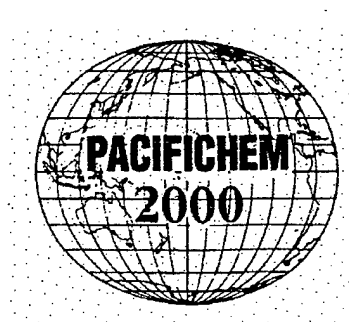
- 001, Reactive Intermediates and Unusual Molecules; Hideo Tomioka; Sat AM, PM; Sun AM, Eve  
 007, Chemistry of the Organic Solid State: Synthesis, Structure and Reactivity; Fumio Toda; Mon AM, PM, Eve; Tue AM  
 010, Pi-electronic Systems with Novel Structure; Yoshito Tobe; Thu AM, PM; Fri AM, PM  
 012, Strategy for Molecular and Supramolecular Photochemistry; Haruo Inoue; Thu AM, PM; Fri AM, PM, Eve  
 020, New Synthetic Methods in Organofluorine Chemistry; Takeo Taguchi; Thu AM, PM; Fri AM  
 024, New Strategies to Transition Metal Catalyzed or Mediated Organic Synthesis; Hideo Kurosawa; Fri PM; Sat AM, PM; Sun AM, PM; Mon AM  
 029, New Developments in Organic Radical Chemistry; Ilhyong Ryu; Thu AM, PM; Fri AM  
 030, Prospects for Automated Solution-Phase Synthesis in the 21st Century; Jun-ichi Yoshida; Mon PM; Tue AM  
 035, Photoremoveable Protecting Groups and Caged Compounds: Principles and Applications; Richard Givens; Sun Eve; Mon AM, PM, Eve; Tue AM  
 042, Natural Products Chemistry: Biological Activity and Synthesis; Daisuke Uemura; Fri Eve; Sat AM, PM; Sun AM, PM, Eve  
 052, Organic and Combinatorial Chemistry on Solid Supports; Takeshi Takahashi; Fri PM; Sat AM, PM  
 060, Phase-Transfer Catalysis; Tadatomi Nishikubo; Thu AM, PM; Fri AM  
 065, Discovery and Development of Asymmetric Synthesis and Chiral Technology; Ichiro Shinkai; Thu AM, PM; Fri AM, PM, Eve; Sat AM, PM; Sun AM, PM, Eve  
 066, New Developments in Heterocyclic Chemistry; Mitsuo Komatsu; Sat AM, PM; Sun AM, PM, Eve  
 110, Marine Natural Products Chemistry; Roy Okuda; Mon AM, PM, Eve; Tue AM  
 122, Molecular Oxygen and Organic Peroxides in Chemistry and Biology; Edward Clennan; Fri PM; Sat AM, PM  
 123, Organic Reactions in Aqueous Media; T.H. Chan; Thu AM, PM; Fri AM, PM  
 128, Free Radicals: From Molecules to Materials; Robin Hicks; Sun PM; Mon AM, PM; Tue AM  
 133, Organic and Biological Electrochemistry: Fundamentals and Applications; Jean Lessard; Sat AM, PM; Sun AM, PM  
 138, Biocatalysis in Organic Synthesis; Jon Stewart; Mon AM, PM; Tue AM  
 141, Organic Photochemistry; Howard Zimmerman; Fri Eve; Sat AM, PM; Sun AM, PM, Eve; Mon Eve  
 144, Cycloaddition and Annulation Strategies; Rick Danheiser; Thu AM, PM; Fri AM, PM  
 163, Bioorganic Reaction Mechanisms; John Richard; Thu AM, PM; Fri AM, PM, Eve  
 175, Use of Chemical Information in Organic Synthesis; Guenter Grethe; Mon AM, PM; Tue AM  
 182, Transition Metal Facilitated Reactions Leading to Organic Heterocycles; P. Wyn Jennings; Sun Eve; Mon AM, PM, Eve; Tue AM  
 208, Boundary Between Long Bond and Short Non-Bonds; Jay Siegel; Sun AM, PM

## AREA 10: Physical and Theoretical

SW

- 004, Solvated Molecules and Ions: from Clusters to Condensed Phases; Dennis Salahub; Sat AM; Sun AM, PM; Mon AM, PM; Tue AM  
 016, Recent Progress in the Science and Technology of Fullerenes and Nanotubes; Yohji Achiba; Thu AM, PM; Sat AM; Sun AM; Mon AM  
 022, Chemical Applications of Synchrotron Radiation; Toshiaki Ohta; Thu AM, PM; Fri AM  
 025, Nonlinear Dynamics in Chemistry; Kenneth Showalter; Fri Eve; Sun AM, PM, Eve; Mon Eve  
 033, Electrochemical Surface Science at Molecular/Atomic Resolution; Kohei Uosaki; Thu AM; Fri AM, Eve; Sat PM  
 069, Solvation Structure and Reactivity in Supercritical Fluids; Okitsugu Kajimoto; Fri AM, PM; Sat AM, PM  
 071, Mathematical Characterization of Structure and Properties of Molecules; Haruo Hosoya; Sun PM; Mon AM  
 077, Ordered Molecular Films for Nano Electronics and Photonics; Atsushi Koma; Fri AM, PM, Eve; Sat PM  
 078, New Frontiers in Chemical Reaction Dynamics; Hiroki Nakamura; Sat AM, PM; Mon AM, PM; Tue AM  
 103, Laser Control and Manipulation of Molecules; Andre' Bandrauk; Thu AM, PM; Sat AM; Sun AM, PM  
 108, Materials Chemistry on Oxide and Carbide Surfaces; Charles Campbell; Sun PM; Mon AM, PM; Tue AM  
 114, Fluids at Interfaces; Douglas Henderson; Thu AM, PM; Fri Eve; Sun AM, Eve  
 125, Computational Quantum Chemistry: Theoretical and Experimental Perspectives; John Goddard; Thu AM, PM; Fri AM, PM, Eve; Sat AM, PM; Sun AM  
 136, Advances in Quantum Monte Carlo; Stuart Rothstein; Mon AM, PM, Eve; Tue AM  
 146, Science and Technology of  $TiO_2$  Photocatalysis; Abhaya Datye; Fri PM Sat AM, PM  
 147, Structure and Dynamics of Photogenerated Intermediates in Solution: Vibrational and Electronic Studies; Terry Gustafson; Thu AM, PM; Fri AM, PM  
 167, Nanomaterials: Synthesis, Characterization and Catalysis; G.A. Somorjai; Sun PM, Eve; Mon PM, Eve  
 168, Surfactant Science and Technology; John Scamehorn; Sun AM, PM; Mon PM  
 179, Physical Chemistry/Chemical Physics of Ion Channels; P.C. Jordan; Sun PM; Mon AM, PM, Eve  
 191, Structure, Dynamics, and Reactions of Small Clusters; Elliot Bernstein; Thu AM, PM; Fri AM, PM

198, Photon and Electron Induced Processes on Surfaces; Hai-Lung Dai; Thu PM; Fri PM; Sat PM; Sun AM  
210, Large Molecule Vibrational Dynamics; Charles Parmenter; Fri AM, PM, Eve; Sat PM  
215, Metal-Metal and Metal-Ligand Interactions; Benoit Simard; Mon AM, PM; Tue AM



***Symposium on Plasma Chemistry and  
Technology for Green Manufacturing,  
Pollution Control, and Processing Applications  
(#211)***

PROGRAM- Renaissance Ilikai Hotel

Session I- *Plasma Pollution Control*      Thursday, 14 December, Afternoon

**Dr. John Hoard**, "Plasma-catalyst for diesel emission reduction" (20 min)

**Dr. Toshiyuki Yamano**, "Decomposition of NO by microwave- induced plasma under atmospheric pressure" (15 min)

**Dr. Atsushi Ogata**, "Removal of dilute benzene using zeolite-hybrid plasma reactor" (15 min)

**Prof. Martin Gundersen**, "Pulsed plasmas for diesel emission reduction" (20 min)

**Prof. Tetsuji Oda**, "Contamination control of air by using non-thermal plasma with catalysts" (20 min)

**Dr. Young-Hoon Song**, "Synergistic effects of non-thermal plasma and catalysts on decomposition of pollutant gases" (15 min)

**Dr. Andrzej Miziolek**, "Silent discharge model development for NO conversion" (15 min)

**Dr. Koichi Mizuno**, "Decomposition of fluorocarbons by an inductively-coupled r.f. plasma torch" (15 min)

**Prof. Moo Been Chang**, "Evaluation of dioxin emissions from two MSC incinerators in Taiwan" (20 min)

**Prof. Michael Hoffmann**, "Kinetics and mechanisms of E. coli disinfection in a pulsed plasma discharge reactor" (15 min)

**Dr. Louis Rosocha**, "Small-pilot-scale field demonstration on the control of atmospheric emissions from jet-engine test facilities using a corona radical shower non-thermal plasma reactor" (15 min)

**Prof. Toshiaki Yamamoto**, "Removal of NOx from diesel engine exhaust using plasma-chemical process" (20 min)

Session II- *Green Chemistry and Novel Applications* Friday, 15 December,  
Afternoon

**Prof. Toshikazu Ohkubo**, "Two-dimensional NO concentration by uv pulse laser LIF diagnostic system in a DC positive streamer corona" (20 min)

**Prof. Masayuki Itoh**, "*Ab initio* calculation of ion-induced water nucleation by dividing model of cluster energy" (15 min)

**Prof. Ko-Shao Chen**, "Hydrophilic modification of polypropylene particles by plasma and graft polymerization techniques" (15 min)

**Prof. Akira Mizuno**, "Low temperature NO<sub>x</sub> reduction process with combination of pulsed discharge and catalyst" (20 min)

**Dr. Shigeru Kado**, "Methane activation with direct pulse discharge" (15 min)

**Prof. Shigeru Ono**, "Study of waste plastic disposal by means of H<sub>2</sub>O microwave plasma process" (15 min)

**Prof. Masayuki Sato**, "Wastewater treatment using pulsed discharge in water" (20 min)

**Dr. Yukimi Ichikawa**, "Plasma processing technologies for thin film solar cell production" (15 min)

**Prof. Bruce Locke**, "The degradation of organic compounds by aqueous phase pulsed corona discharge" (20 min)

**Dr. Kuniko Urashima**, "Removal of mixed PFCs by a full scale ferro-dielectric packed bed non-thermal-adsorbent hybrid reactor" (15 min)

**Dr. Jerzy Mizeraczyk**, "Influence of the pellet properties on NO<sub>x</sub> removal in a packed-bed plasma reactor" (20 min)

**Dr. Shigeru Futamura**, "Control of VOC decomposition behavior in air with silent discharge plasma and catalysts" (15 min)

Summary of Symposium: Prof. Jen Shih Chang